Inkjet Printing of Non-Volatile Rewritable Memory Arrays

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Abstract

Inkjet printing of all-polymer non-volatile rewritable memories was demonstrated. A polymeric ferroelectric material sandwiched between two electrically conductive layers formed the memory cell. Inkjet printing of the electrodes was performed with PEDOT-PSS and the active layer was printed with a ferroelectric polymer. Both fluids were modified for high quality jetability in Xaar's XJ126 binary printheads. The test device contained memory arrays of up to 100 bit with a design rule of 200µm wide electrode lines and 1mm line spacing. A pinhole-free ferroelectric layer of 120nm thickness allowed switching of the memory devices at voltages below 20V within 1ms. Large signal-to-noise ratios were recorded even after 10^5 read-write cycles. Target areas for this technology are low-density memories on flexible plastic substrates or on special papers. Application areas are tag memories, anti-counterfeiting and smart packaging.

Introduction

Printed electronics is a rapidly growing field of research and development. Printed transistors and display elements are the most commonly reported devices [1, 2, 3]. Many electronic functions do, however, need memory and in particular non-volatile memory. Very little has been reported in that field. At a recent printed electronics conference only one out of 34 presentations was explicitly devoted to memories [4].

Most publications on memory cells deal with fuse-type read-only memories (ROM) [5]. Integrated circuits based on printed organic transistors have been reported, which could potentially be used for random access memories (RAM) [1, 2].

The present work describes a random access memory based on a ferroelectric polymer. As will be shown below, such organic ferroelectric RAMs can be manufactured by inkjet printing. In view of the specific virtues of inkjet printing (digital, non-contact, etc) a wide range of applications, particularly in the packaging industry, can be addressed.

Inkjet printing is limited in resolution, so that the achievable storage density cannot be compared with silicon-based memory chips. However, 1 kbit memory arrays can be readily produced, for use in applications such as security, certification of ownership, brand protection etc.

The work presented here aims to show the basic functionality of fully inkjet printed ferroelectric memories. The test layout contains a 100 bit memory array. The device is an all-organic memory, i.e. the materials are mechanically flexible so that they could be successfully printed and operated even on cheap flexible materials like PET.

Principle of non-volatile ferroelectric memories

Ferroelectric materials are capable of obtaining permanent electrical polarization. In addition to a dielectric response, these materials also have a non-linear ferroelectric response to an applied electric field. The ferroelectric response is, in its simplest form, characterised by a coercive field and a remnant polarization. The externally applied field needs to exceed the coercive field to make the dipoles change polarization state, or "switch". The amount of charge per unit area provided by the displacement current for the switching is called polarization [6].

The remnant ferroelectric polarization by itself provides a means for memory function. The polarization state can be set and detected by an external electric field, and is bistable, i.e. it will remain in either of the two polarization states even when the electric field is not applied. This makes the material suitable for a non-volatile rewritable digital memory circuit.

Such memory devices have been proposed in the research literature as well as being commercially manufactured by different companies. Inorganic ferroelectrics have been integrated with Si-circuits by e.g. Ramtron and Fujitsu, to produce non-volatile memories of up to 1 Mbit [7]. However, organic polymer ferroelectrics are of more interest for printed electronics.

Several polymer types with ferroelectric properties have been reported; poly(vinyldiflouride) (PVDF) and its copolymers with trifluoroethylene (PVDF-TrFE), odd nylons, polyamides and polyurea are some examples [8].

The present work is based on a fluoropolymer. This material is soluble in organic solvents and can readily be deposited from solution by a variety of deposition techniques. In this way a uniform wet film is deposited and evaporation of the solvent leaves a thin homogeneous polymer film. The film is subsequently thermally annealed to increase crystallinity, forming a ferroelectric material.

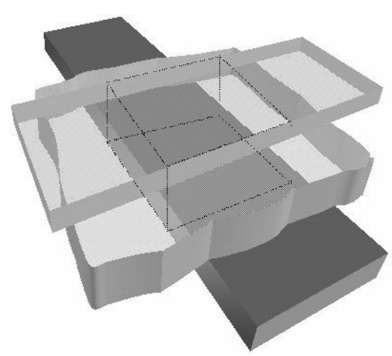


Figure 1. *Ferroelectric memory cell schematically shown by the ferroelectric film sandwiched between crossing electrodes.*

An electrical field is applied across the ferroelectric layer by top and bottom electrodes. The electrodes can be produced in the form of lines, oriented perpendicular to each other, and the memory cell defined by the intersection of the lines. This kind of memory device structure is schematically shown in Figure 1. The electrodes can be metallic or semiconducting, e.g. conducting polymers can be used.

Basic layouts and test designs

A layout has been designed to test and evaluate different memory array sizes, as well as single memory cells and test features e.g. for measurement of conductor line resistivities. Figure 2 shows part of this memory array test pattern, which includes a 100 bit memory array and some 16- and single-bit memories.

The sequence for producing the memory test structures was similar for all printed memories, with all layers deposited by inkjet printing. The bottom electrodes were first of all printed with the conductive polymer PEDOT-PSS. After drying and thermal annealing of the bottom electrodes, the ferroelectric polymer was laid down as a continuous layer covering the whole area of the electrode lines, but leaving the contact pads uncovered. After annealing of the ferroelectric film, the top electrodes were printed with PEDOT-PSS oriented perpendicular to the bottom electrodes, and once more dried and annealed.

As a final step, silver ink was inkjet printed onto the contact pads. This silver layer was not required for the functionality of the memory cells, but it allowed frequent reproducible contacts with test probes.

This kind of relatively simple test pattern, with a low number of bits, as shown in Figure 2, demonstrates the feasibility of the printing process for polymeric memory arrays. Higher memory densities can be achieved by using smaller line pitches and multi-layer approaches.

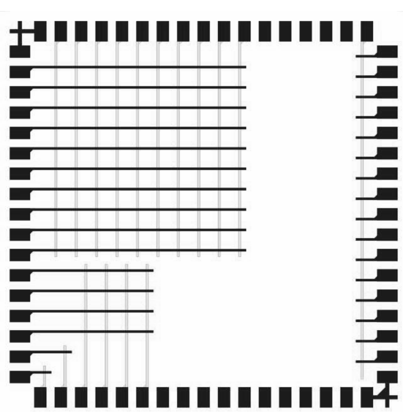


Figure 2. *Layout for part of the memory array test structure*

Typical drying and annealing conditions used to obtain the desired conductivities and functionalities of the different layers were 20-30 min at 120 °C for both the PEDOT-PSS electrodes and the ferroelectric film, and several hours at 120 °C for the inkjet printed Ag-contact pads. The maximum temperatures were limited to this range to avoid thermal damage to the substrates.

The alignment from layer to layer was realized using registration marks and an optical vision system on the printing station with manual correction of the alignment offset. In this way it was possible to achieve alignment accuracies better than 100µm, which was sufficient for the tested layouts.

Inkjet printing process for the functional materials

Inkjet printing of the ferroelectric memory cells was carried out with Xaar's XJ126-50 and XJ126-80 binary printheads, with 126 channels, delivering drop volumes of 50 and 80pl, respectively. These are piezoelectric drop-on-demand printheads, utilizing a shear-mode, shared-wall principle [9, 10]. Xaar's printheads work with a wide range of fluids and are thus most useful for industrial applications in electronics, displays etc.

Different from earlier work on inkjet printing of PEDOT-PSS dispersions, which was carried out with a development type PEDOT from AGFA [11], commercial Baytron P Jet HC from H.C. Starck was used for the present work, and further modified (see below). Printheads with a special passivation were used for printing the corrosive PEDOT-PSS fluid.

The ferroelectric polymer (TFE proprietary material), a fluid containing high molecular weight material, had to be modified as well to provide the quality of drop formation and printing needed for the manufacturing of the memory device.

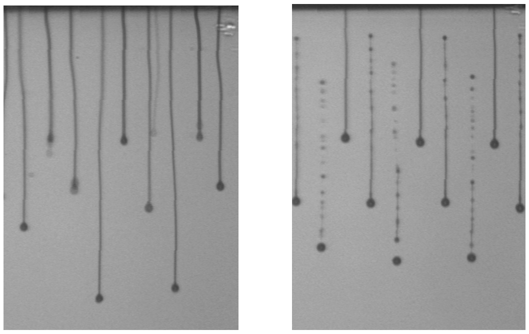
Jetting process for the electrode materials:

Baytron P Jet HC, a water-based dispersion of PEDOT-PSS, was adapted for the Xaar-type printheads in order to enable improved jetting performance. As a typical example, such a modified formulation for PEDOT-PSS dispersions contained 90% Baytron P Jet HC, pH-adjusted to a nearly neutral range using DMEA (dimethylethanolamine), 10% ethylene glycol or glycerol, and 0.05% to 0.1% of the surfactant Dynol 604 (Air Products). With these adapted formulations, and utilizing a modified driving waveform for the printhead, regular and stable drop formation with a minimum amount of satellite drops was observed at jetting frequencies up to 6.7kHz.

Inkjet printing of the ferroelectric polymer

Different versions of the ferroelectric polymer, dissolved in a range of organic solvents, were tested with respect to jetability and printing performance.

It was found that a number of solvents were suitable for the jetting process, but that the molecular weight (MW) of the ferroelectric polymer had to be limited in order to allow reliable jetting. Figures 3a and 3b shows drop formation with suspensions of ferroelectric polymers with different MW. In these figures, the nozzle plate is visible at the top of the photograph, and the drops, ejected in three subsequent phases, were imaged in flight; the distance from top to bottom in the photos is around 1.5mm. In the case where fractions with very high MW were present (Figure 3a), the drops formed very long tails that broke up very late, or sometimes did not break at all and pulled the drops back towards the nozzle plate. In the case when the MW was limited (Figure 3b) drops could be reliably jetted at frequencies up to 3kHz, even if some satellite drops were formed.



(a) (b)

Figure 3. Inkjet drop formation with solutions of ferroelectric polymers: (a) with high MW fractions present; (b) no high MW fractions

Properties and characteristics of inkjet printed memory arrays

Dimensions, layer interfaces and feature sizes

To produce the first demonstrator memory structures as shown in Figure 2, a conservative design rule of 200-250µm linewidth and about 1mm spacing was chosen for the electrodes of the memory arrays.

The challenge in producing a sandwich structure for the memory cell, consisting of a bottom-electrode, the ferroelectric film and a top-electrode, was to engineer the surface morphology and interfaces between the layers in such a way that smooth surfaces without spikes or pinholes were formed, which could cause shorts or malfunctions of the memory devices. In addition it was important to achieve the necessary pattern fidelity of the electrode pattern, while maintaining smooth edges with gradual increase in thickness at the line edges.

In Figure 4, a 220µm wide and 200nm thick electrode line is shown, printed with the modified Baytron P Jet HC dispersion as described above. As the line profile in the right part of the image shows, it was possible to print the electrode lines in such a way that a smooth thickness gradient was maintained and no spikes or steep cross-sectional profiles were produced. Atomic force microscopy analysis showed that the rms value for the roughness of these electrode line surfaces was in the order of 4nm. This was also facilitated by filtering the PEDOT-PSS dispersion through a 0.45µm or 1µm syringe filter to remove larger particles. In comparison, for a different, non-optimized PEDOT dispersion an rms of about 18nm was found, which resulted in a substantial increase in the number of shorts and malfunctioning memory cells.

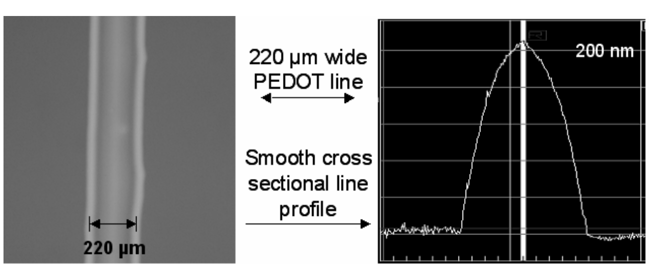


Figure 4. Optical image and line profile of an electrode line inkjet printed with a modified Baytron P Jet HC dispersion

From the electrical characterization a sheet resistance of about 1kΩ/sq. was measured for a single-pass printed electrode layer, which was sufficient to operate the memory arrays.

The need for smooth surfaces at the interfaces becomes particularly apparent when considering that the target thickness of the ferroelectric film was of order 120nm, in order to be able to drive the memory with voltages below 20V. With the polymer solutions described above, it was possible to produce uniform, smooth and defect-free ferroelectric films, which also formed the interface for printing of the top electrode. Apart from changing the solid content of the polymer solution, it was possible to vary the thickness of the film by changing the pattern density, i.e printing of pattern with an area coverage of 50% or 75%, while still achieving continuous lines and layers.

In Figure 5 a fully inkjet printed memory test structure with a 100 bit array and some smaller memory cells and test structures (based on the layout in Figure 2) is shown. The substrate for the memory array was a flexible polymer foil (PET). The size of the test piece can be seen in the right image in Figure 5, the approximate dimensions are 25×25mm. These dimensions and memory sizes could readily find applications in e.g. product identification or anti-counterfeiting, where the memories could be attached as separate labels.

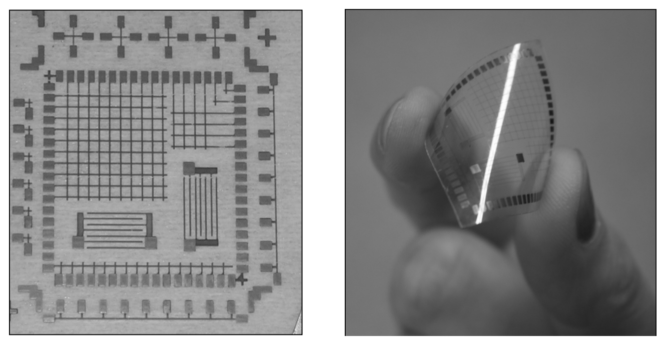


Figure 5. Fully inkjet printed ferroelectric memory arrays, including a 100 bit RAM memory and some smaller memory cells and test features

Characterization & properties of memory arrays

Information in the memory cell can be stored in either of the two polarization states. By applying certain sequences of voltage pulses to the electrodes the polarization can be changed and set to the desired state. These pulse sequences are the read and write operations. Amplitude and length of the pulses are specific for a certain device geometry. For the current printed samples the ferroelectric response of a memory cell was fully recorded in 1 ms, and the integrated displacement current resulted in a polarization of approximately 10µC/cm^2. Figure 6 shows a typical measurement where a voltage pulse was applied to the memory cell (0-1 ms) and changed the polarization state. This was observed from the large response during time 0-1 ms. Next the voltage was zeroed during the time interval between 1-2 ms and the capacitive (non-ferroelectric) charge was released. During time 2-3 ms a new pulse was applied (same polarity as the first pulse) and the response was only capacitive since the polarization was not reversed. Only a small response was recorded during 2-3 ms. The pulses were repeated, but with a different polarity, and resulted in the corresponding responses, namely first a switch of the polarization (4-5 ms) and then a non-switch (6-7 ms).

The recorded signal clearly shows that the switch and non-switch responses (“1” and “0”) are easily distinguished and the diagram furthermore shows a large signal-to-noise ratio. The tests also showed that repeated switching for 10^5 cycles did not result in any significant degradation. This performance is expected to be adequate for printed electronics applications.

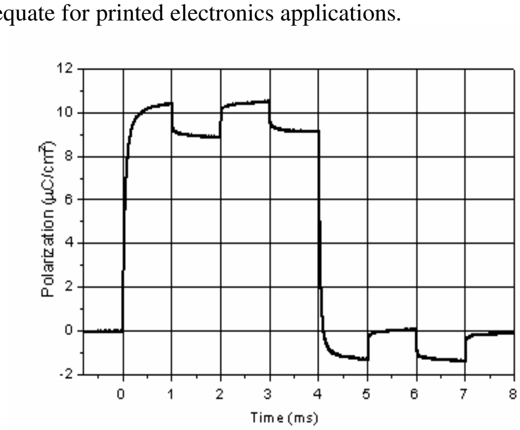


Figure 6. *Ferroelectric response of a printed memory cell. Positive voltage pulses are applied at 0-1 ms and 2-3 ms*

A ferroelectric memory device can be designed as a passive array. This means that the memory array doesn’t contain more than the memory cells themselves. All other circuitry, such as the transistors, are placed outside the array. The memory cells are accessed and addressed by applying suitable voltage schemes to the electrode lines which form an array of crossing points. The electrodes are commonly referred to as wordlines and bitlines.

The printed memory array was connected to a home-made memory tester by contacting the Ag-ink pads. The memory tester essentially consists of control electronics to apply correct voltages to the various word- and bitlines, and sense amplifiers to measure the charges from a cell during read. The voltages applied to word- and bitlines depend on whether it is a read or write operation and, in the case of a write operation, what data should be written. The memory tester is controlled by a computer through a USB interface, and is designed for passive ferroelectric matrixes up to 1 kbit (32x32 bits).

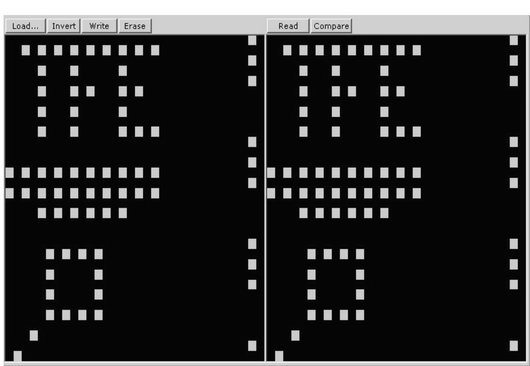


Figure 7. *Bitmap of written and read data in a 100 bit inkjet printed memory array*

In Figure 7 a screenshot for such a memory test is shown, where a pattern of 100 bit was written (left part of the image), and the stored information correctly read out again in a second step, as can be seen in the right part of the image.

Conclusions

A fully functional 100 bit passive RAM was inkjet printed. All three layers, i.e. two electrode layers and a ferroelectric film, were polymeric, thus resulting in an all-organic RAM memory. The inkjet printed silver nano-particle pads were merely added to provide good electrical contact during the frequent test cycles. Printing the ferroelectric layer sandwiched between two electrode layers required modification to both the PEDOT-PSS as well as the high molecular weight polymer ferroelectric fluid, in order to obtain good jetability and printing with high pattern fidelity. Most challenging was the printing of the ferroelectric layer. It was possible to print such pinhole-free layers on top of the 200nm thick and 220µm wide PEDOT-PSS bottom electrodes. The 120nm thickness of the ferroelectric layers allowed a switching voltage below 20V.

Information is stored by polarizing the ferroelectric material. No voltage was needed to maintain the information, thus providing a non-volatile memory. The ferroelectric memory cell with the present dimensions of 200µm square area and 120nm ferroelectric film thickness could be switched between ‘0’ and ‘1’ states in less than 1ms with large signal-to-noise ratio. Up to 10^5 read and write cycles did not degrade the performance significantly, enabling industrial applications of this memory.

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Author Biography

Wolfgang Voit is member of the Advanced Application Technology department at Xaar. He received his diploma from the University of Applied Sciences in Regensburg, Germany. In 1997 he joined MIT Inkjet, Järfälla, Sweden, and Xaar in 1999. In the past 9 years he gained thorough experience in both inkjet printhead technology as well as developing new inkjet applications, specifically in the area of inkjet printing of functional fluids for manufacturing of displays, sensors and memories.